

RECENT ADVANCES IN HIGH-PERFORMANCE DIRECT METHANOL FUEL CELLS

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Introduction

Direct methanol fuel cells for portable power applications have been advanced significantly under D. ARPA- and ALC-sponsored programs over the last five years. A liquid-feed direct methanol fuel cell developed under these programs, employs a proton exchange membrane as electrolyte and operates on aqueous solutions of methanol with air or oxygen as the oxidant. Power densities as high as 320 mW/cm² have been demonstrated. Demonstration of five-cell stack based on the liquid-feed concept have been successfully performed by Giner Inc. and the Jet Propulsion Laboratory. Over 22000 hours of life-testing have been completed on these stacks. These fuel cells have been also been demonstrated by USC to operate on alternate fuels such as trimethoxymethane, dimethoxymethane and trioxane. Reduction in the parasitic loss of fuel across the fuel cell, a phenomenon termed as "fuel crossover" has been achieved using polymer membranes developed at USC. As a result efficiencies as high as 40% is considered attainable with this type of fuel cell. The state-of-the-art has reached a point where it is now being actively considered for stationary, portable and transportation applications. The research and development issues have been the subject of several previous articles [1-5] and the present article is an attempt to summarize the key advances in this technology.

The Liquid-Feed Direct Methanol Fuel Cell

The heart of the fuel cell is a membrane-electrode assembly consisting of two catalyzed electrodes bonded to either side of a proton-exchange membrane similar to that used in the low-temperature hydrogen-oxygen fuel cells. Nafion 117 is an example of such a membrane. The anode employs platinum-ruthenium as the catalyst and sustains the electro-oxidation of methanol to carbon dioxide. The cathode employs platinum as the catalyst and sustains the electro-reduction of air/oxygen to water. During operation, an aqueous solution of methanol (about 3 v/v %) is circulated past the anode. The carbon dioxide produced at the anode is separated from the liquid stream and the solution is re-circulated. The fuel cell has been operated over between 15° and 120°C, the efficiency and power densities being higher at the higher temperatures. The typical operating point for many applications could be in the range of 50- 95°C. The fuel cell can operate at ambient pressure. The overall simplicity of this concept renders this fuel cell very attractive from a system perspective. A demonstration of the system concept for D. ARPA applications is now in progress at JPL and Giner Inc. Briefly, the performance of these fuel cells is determined by the activity of the anode catalyst, the methanol permeability and ionic conductivity of the membranes, cathode structures and method of preparation of membrane-electrode assemblies. Advances in each of these areas leading to the current levels of performance are summarized in the following.

Anode Performance:

Platinum-ruthenium is found to be the most efficient catalyst for the electro-oxidation of methanol. These catalysts usually consist of an alloy of platinum-ruthenium with small amounts of oxide in a reduced state and the best performance is found to be attained when the composition corresponds to a molar ratio of 50:50 (Pt:Ru). Catalysts separately prepared at the Jet Propulsion Laboratory and Giner Inc., by quite different methods have been found to have similar performance. Significant improvements in catalyst performance and utilization have been by modifications of preparation procedures. These catalysts are resistant to poisoning unlike pure platinum catalysts. The anode polarization curves for various concentrations of methanol have been derived from full cell performance data and demonstrate that very high current densities are possible at the anode using platinum-ruthenium catalysts. The typical operating electrode potential for the anode is in the range of 0.35-0.38 V for 400-500 mA/cm² at 90°C. Also, these results demonstrate that performance of the anode at high current densities is limited significantly by the mass transport of methanol rather than the activity of the catalyst. This situation presents a significant advance over the prior-art methanol fuel cells which could not operate at a tenth of the present power levels. Since mass transport of methanol and the kinetics of oxidation are enhanced by increasing temperature, higher performance can be attained by increasing the operating temperature of the fuel cell. The typical operating point for most applications is in the range of 55-95°C.

Cathode performance:

The cathode can be operated on air/oxygen. The fuel cells are capable of operating on air at ambient pressures. Figure 1 shows the typical performance differences for operation on air and oxygen.

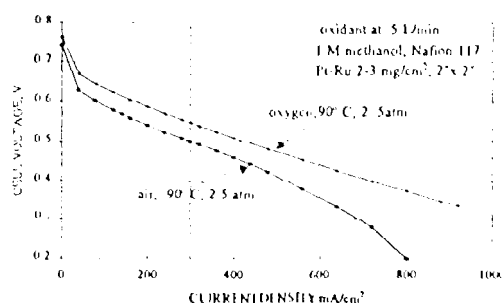


Figure 1. Performance of direct methanol fuel cell operating on air and oxygen

Current densities as high as 600 mA/cm² can be sustained on near-ambient pressure air. These results present significant improvement over the prior-art fuel cells based on methanol. From the point of the lowering overall system size and increasing system efficiency, the operability on ambient pressure air at stoichiometric rates of less than five is very important. The performance of the cathode is dependent on the flow rate of air. This performance characteristic is caused by the differences in the rate of removal of water produced at the cathode at various flow rates. The use of thin hydrophobic backing layers, ultra-thin catalyst layers and modified flow fields are found to have a beneficial effect on the performance of the cathode and are currently being pursued by JPL and Giner Inc.

Membrane-Electrode Assemblies:

The key step in the method of preparation of membrane-electrode assemblies for this type of fuel cell involves the formation of a catalyst-membrane interface that presents a large electrochemically active surface area and high protonic conductivity. Typically, the preparation of such membrane-electrode assemblies involve the formation of composite electrode layers

consisting of catalyst and proton-conducting material and hot-bonding of these layers to the proton-exchange membrane such as Nafion 117. Considerable differences in performance can arise from the methods employed. Enhanced performance of direct methanol fuel cells arising from the direct application of catalyst to the membrane are shown in Figure 2.

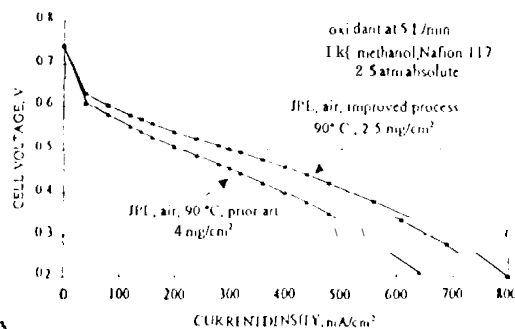


Figure 2. Performance of direct methanol fuel cell with reduced loading, and improved process for fabricating membrane electrode assemblies.

These new methods allow the formation of ultra-thin catalyst layers resulting in improved mass transfer and increased catalyst utilization.

Methanol Crossover:

Methanol crossover from the anode to the cathode results in consumption of fuel and also impacts the performance of the cathode causing the cell to operate at a lower overall efficiency. The crossover rate is largely determined by the permeability of the membrane and electrode structures to methanol. Nafion 117 present high ionic conductivity but is also highly permeable to methanol. Nafion membranes with higher equivalent weight have usually lower methanol permeability but also reduced ionic conductivity. Thus the development of membranes with low methanol permeability with high ionic conductivity has been an important effort. The recent results from USC demonstrate that such membranes can be developed. Figure 3 presents data on the relative methanol permeability of new membranes and Nafion 117. These new membranes also possess the high ionic conductivity of Nafion 117. The new membranes are expected to be less expensive than the state-of-art Nafion membranes. The implementation of these membranes into actual fuel cells is being currently pursued at JPL and the initial results show that the electrical performance approach that attained with Nafion.

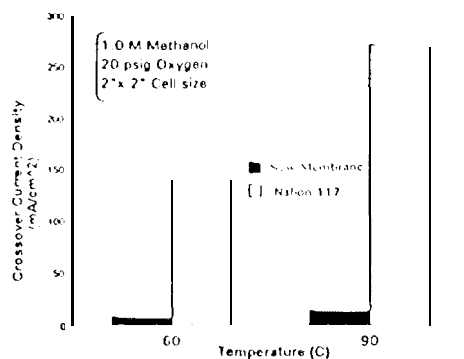


Figure 3. Relative methanol permeability and crossover rates observed with Nafion and newly developed membranes

Stacks and Systems:

Five-cell stacks have been demonstrated at (1) 2.0 and 100 W level by JPL and Giner Inc., respectively with an aim to study stack designs and obtain parametric data on reactant flows and product management in order to be able to achieve a system concept demonstration at the end of December 1996. Performance data on five-cell stacks and membrane-electrode assemblies developed at JPL are presented in Figure 4.

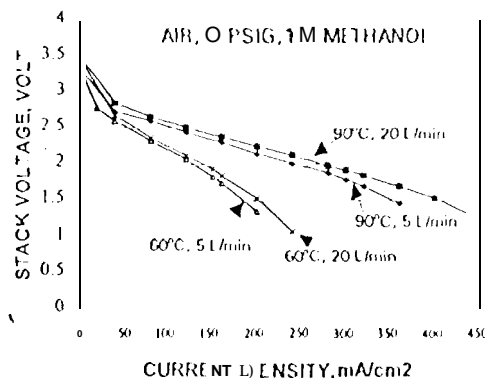


Figure 4. Performance of 5-cell JPL-built direct methanol fuel cell stack at ambient pressure

This data shows the scalability of single cell technology to multi-cell stacks. The development of a 22-cell 60 W stack is presently being pursued for portable power applications. System sizing and thermal management studies are currently under way at JPL and Giner Inc., and power densities in the range of 100 W/kg appear attainable for complete systems.

Lifetesting of fuel cells:

Operation of a five-cell stack over periods extending over 2400 hours has been carried out at Giner Inc. The performance does not show any significant decline over this period. Continuous operation at high power densities for 200 hours at 90°C also indicate no significant concern relating to short-term degradation.

Acknowledgment:

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